

Ba₆WNb₂O₁₄ appears at least in two different polymorphs with the phase transition around 1200°C. The X-ray powder diffraction pattern of high-temperature modification corresponds merely to the niobium homologue of the hexagonal Ba₆WTa₂O₁₄ (ICDD file #35-0187), while the XRD spectra of the low-temperature modification is closely related to the orthorhombic β-Ba₄Nb₂O₉ (ICDD file #35-1155). In order to understand the crystal chemistry governing the formation of Ba₆WNb₂O₁₄, the ceramic prepared by a conventional solid-state reaction, was analyzed by means of X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of microwave dielectric data revealed a low negative coefficient of resonant frequency varying from -25 to -18 ppm/K, dielectric permittivity in the range of 15-20, and the quality factor Qxf distributed over 18 000 GHz.

Keywords: perovskite structures, phase transitions, dielectric materials characterization, TEM, X-ray crystal structure analysis

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Crystallographic direct observation of chemical reactions in a pore

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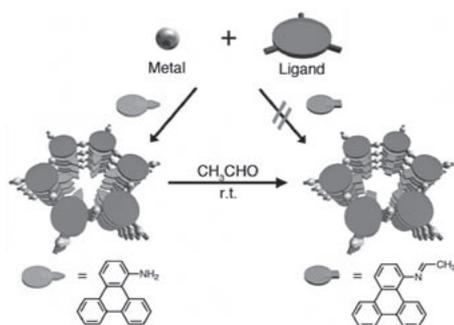
In-situ preparation of labile compounds in a single crystalline state is a unique and effective method for the crystallographic observation.¹ There are, however, several practical problems in this method. Here we utilize the pores of a coordination network. Thanks to the pseudo-solution state in the pores, even bulky substrates can easily interpenetrate into the crystals with keeping single crystallinity. We examined the reaction of acetaldehyde with amines to form acetaldehyde imines that are, normally, easily hydrolyzed or isomerized into enamines.² The aromatic amines were incorporated in the columnar array of aromatic ligands of an as-synthesized porous network complex.³ We also succeeded in observing several condensation reactions of the aromatic amines to produce acylated products in a pore.

References

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Keywords: *in situ* observations, coordination polymers, reactive intermediates

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Phase behavior of block copolymer/inorganic nanocomposites

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Block copolymers offer as versatile platforms for the fabrication of hybrid composites with ordered phases useful for nanotechnology. Success in this area however requires knowledge on the thermodynamic principles that govern the self assembly of the nanoparticles in the polymer matrix and the resulting morphology and the long range order of the nanocomposites. We carried out a systematic study on the phase behavior of block copolymers with well dispersed grafted nanoparticles enthalpically compatible to one of the domains of the block copolymer. The sequestered nanoparticles in the preferred domain have profound effects on the thermodynamically induced microphase separation of the block copolymers. A number of molecular properties such as polymer molecular weight, segment volume fraction, chi parameter and nanoparticle concentration influence the state of dispersion of the nanoparticles and the degree of segregation of block copolymer morphology. In general, the inorganic nanoparticles tend to weaken the degree of segregation and adversely affect the long range order. We have used a simple method of using small molecular weight homopolymer that can sequester in the same domain as the nanoparticles to overcome the adverse effect of nanoparticles and improve the long range order in the nanocomposites. The basis for this approach is that the small polymers would increase the conformational entropy and swell the preferred domain uniformly which leads to a smoothed interface and improved long range order. The uniform swelling of the preferred domain by the small polymers will also enable higher loading of nanoparticles without losing the long range order. The derived phase behavior will have high impact in the design and fabrication of composites for nanotechnology.

Keywords: block copolymer, nanocomposites, small angle diffraction

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From molecular clusters to nanocrystals - Optical and magnetic properties of metal sulfides

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In this talk, I will discuss the transformation of molecular clusters of molybdenum sulfide and arsenic sulfide into novel nanocrystals with new properties. Bulk molybdenum disulfide is known to be a nonmagnetic material. We have synthesized edge-oriented MoS₂ nanosheet-like films that exhibit weak magnetism (similar to 1-2 emu/g) and 2.5% magnetoresistance effects with a Curie temperature of 685 K. The magnetization is related to the presence of edge spins on the prismatic edges of the nanosheets. Spin-polarized calculations were performed on triangular-shaped cluster models in order to provide insight into the origin of magnetism on the edges as well as